Supporting Information

for the manuscript entitled

Ligand Induced Circular Dichroism and Circularly Polarized Luminescence in CdSe Quantum Dots

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UV-vis absorption: UV-vis absorption spectra were collected at 20 °C using a Jasco V-600 UV-vis double beam spectrophotometer equipped with a single position Peltier temperature control system. A quartz cuvette with a 1 cm path length was used for all UV-vis experiments.

Fluorescence: Emission measurements were done at 20 °C using a Varian fluorescence spectrophotomer equipped with a four position Peltier temperature control system using a scan rate of 600 nm/min, excitation wavelength 450 nm, with 5.0 nm excitation slit, and 5.0 nm emission slit. A quartz cuvette with a 1 cm path length was used.

Transmission electron microscopy (TEM): Samples for TEM were prepared by ultrasonic dispersion of the CdSe nanoparticles in toluene and water for the oleic acid and cysteine capped particles respectively. The suspension was then drop-cast onto carbon-coated copper grids and dried in air. Imaging was performed on an FEI Tecnai G2 F20 scanning transmission electron microscope (STEM) operating at 200 kV.

Circular dichroism (CD) and fluorescence detected circular dichroism (FDCD): CD spectra were recorded at 20 °C using a Jasco J-815 spectropolarimeter equipped with a single position Peltier temperature control system. Conditions were as follows: scanning speed 100 nm/min, data pitch 0.5 nm, DIT 1 s, and bandwidth 4 nm. A quartz cuvette with a 1 cm path length was used for all CD experiments. Each CD spectrum was an average of at least fifteen scans. FDCD spectra were recorded at 20 °C using a Jasco J-815 spectropolarimeter equipped with a single position FDCD Peltier temperature control system and a FDCD-465 attachment combining both a cylindrical cell and an elliptical cylinder mirror. Conditions were as follows: scanning speed 100 nm/min, data pitch 0.5 nm, DIT 1 s, bandwidth 6 nm, 580 nm filter, and masks No7. Each FDCD spectrum was an average of at six scans.

Circularly polarized luminescence (CPL): CPL and total luminescence spectra were recorded on an instrument described previously,[1] operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission,[2] a high quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected

by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode. All measurements were performed with quartz cuvettes with a path length of 1.0 cm.

Magic angle spinning solid state NMR (MAS ssNMR): MAS ssNMR experiments were carried out on a 600 MHz Avance III Bruker NMR spectrometer equipped with a 3.2 mm E^{free} triple resonance HCN probe. Three standards (L-cysteine, L-cysteine hydrochloride, tetramethylammonium hydroxide) and L-cysteine capped CdSe QDs were packed into 4 mm Bruker rotors. To prepare the ssNMR sample, L-cysteine capped CdSe QDs were lyophilized overnight from water. One dimensional (1D) ^{13}C ssNMR spectra were acquired using ^{1}H-^{13}C cross-polarization (CP) and ^{1}H decoupling during acquisition. For the CdSe QDs, ^{1}H-^{13}C CP was achieved with a 70-100% ramped 63 kHz ^{1}H and 50 kHz ^{13}C pulses for 2.0 ms. Spectra was acquired for 20-40 ms with 78 kHz of two-pulse phase modulated (TPPM) ^{1}H decoupling. For the standards, 16-128 transients were signal averaged. L-cysteine capped CdSe QDs ^{13}C spectrum took ~19 h to acquire (24,000 transients with 2.7 s recycle delay). Experiments were performed at 26 °C (variable temperature set point) and 8.0 kHz MAS frequency. All spectra were externally referenced to DSS using the adamantane downfield ^{13}C peak at 40.48 ppm.[3] Data were processed with TopSpin.

Synthesis of TOPO/OA-CdSe QDs

TOPO/OA-CdSe QDs were synthesized using a modified literature procedure by Zou et al.[4]

2.9 nm TOPO/OA-CdSe QDs

A reaction mixture of cadmium oxide (CdO, 0.08 g), trioctylphosphine oxide (TOPO, 4.7 g), oleic acid (OA, 1.9 mL) and octadecene (ODE, 17.0 mL) was deoxygenated and heated to 300 °C under a nitrogen atmosphere. Trioctylphosphine selenide (TOPSe) was prepared by deoxygenating a mixture of selenium (0.1 g), TOP (2.1 mL) and ODE (10.0 mL). The mixture was sonicated for 5 min under a nitrogen atmosphere until the selenium powder disappeared. The TOPSe solution was swiftly injected into the hot CdO solution and the reaction mixture was taken out of heat after 40 s and poured into chilled toluene (40 mL). The QDs were purified by two cycles of precipitating with 5:1 absolute ethanol / toluene respectively while centrifuging each time at 8,000 rpm for 10 min.

Synthesis of OA-CdSe QDs

OA-CdSe QDs were synthesized using a modified literature procedure by Zou et al.[4]

2.5 nm OA-CdSe QDs

A reaction mixture of cadmium oxide (CdO, 0.08 g), oleic acid (OA, 10.0 mL) and octadecene (ODE, 17.0 mL) was deoxygenated and heated to 300 °C under a nitrogen atmosphere. Trioctylphosphine selenide (TOPSe) was prepared by deoxygenating a mixture of selenium (0.1 g), TOP (2.1 mL) and ODE (10.0 mL). The mixture was sonicated for 5 min under a nitrogen atmosphere until the selenium powder disappeared. The TOPSe solution was swiftly injected into the hot CdO solution and the reaction mixture was taken out of heat after 6 s and poured into chilled toluene (40 mL). The QDs were purified by two cycles of precipitation with a 5:1 absolute ethanol / toluene ratio respectively while centrifuging each time at 8,000 rpm for 10 min.

Synthesis of 2.9 nm to 5.3 nm OA-CdSe QDs

The synthesis of 2.9 nm to 5.3 nm OA-CdSe QDs was similar to 2.5 nm OA-CdSe QDs with slight modifications in the synthetic conditions as shown in the Table S1.

Table S1: *Modifications in synthesis of OA-CdSe QDs, Ø = 2.9 nm to 5.3 nm*

OA-CdSe	**Modification in synthetic procedure**		
Ø	**reaction time**	**temperature**	**quenching**
2.9 nm	18 s	300 °C	reaction mixture was poured into chilled toluene (40 mL)
3.3 nm	42 s	300 °C	reaction mixture was poured into chilled toluene (40 mL)
3.7 nm	115 s	300 °C	reaction mixture was poured into chilled toluene (40 mL)
4.2 nm	95 s	256 °C	reaction mixture was poured into chilled toluene (40 mL)
4.5 nm	95 s	256 °C	reaction mixture was left to cool to RT
4.9 nm	182 s	263 °C	reaction mixture was left to cool RT
5.3 nm	555 s	275 °C	reaction mixture was left to cool to RT

Synthesis of cysteine-CdSe QDs from TOPO/OA- CdSe QDs by ligand exchange

Synthesis of 2.9 nm L-cysteine-QDs from TOPO/OA-CdSe QDs

L-cysteine hydrochloride monohydrate (0.2 g) was dissolved in DI water (20 mL, [L-Cys] = 0.056 M). The pH of the resulting solution was adjusted to 12.0 with tetramethylammonium hydroxide pentahydrate (TMAH). A solution of TOPO/OA-CdSe QDs in toluene (12 mL, 0.019 mM) was added to the cysteine solution and the reaction mixture was deoxygenated. The reaction mixture was stirred at room temperature under nitrogen in the absence of light for 24 h. The L-cysteine capped QDs transferred to the

bottom aqueous phase. The reaction mixture was left to stand for 1 h to allow the phases to separate. The bottom aqueous layer was taken out with a syringe and purified by precipitation with acetone/DI water (8:1 respectively). This was centrifuged at 8,000 rpm for 10 min and the supernantant was decanted and the precipitate was redissolved in DI H_2O (2 mL). This was precipitated with acetone again and centrifuged at 8,000 rpm for 10 min. The supernatant was decanted and the precipitate was dissolved in DI H_2O and stored in the dark.

Synthesis of 2.9 nm D-cysteine-QDs from TOPO/OA-CdSe QDs

D-cysteine CdSe QDs were synthesized using the same procedure as for L-cysteine CdSe QDs except that D-cysteine hydrochloride monohydrate was used.

Synthesis of cysteine-CdSe QDs from OA-CdSe QDs by ligand exchange

Synthesis of 2.5 nm L-cysteine-CdSe QDs

L-cysteine hydrochloride monohydrate (0.2 g) was dissolved in DI water (20 mL, [L-Cys] = 0.056 M). The pH of the resulting solution was adjusted to 12.0 with tetramethylammonium hydroxide (TMAH). A solution of OA-CdSe QDs in toluene (12 mL, 0.03 mM, A_{exc} = 0.85) was added to the cysteine solution and the reaction mixture was deoxygenated. The reaction mixture was stirred at room temperature under nitrogen in the absence of light for 24 h. The L-cysteine capped QDs transferred to the bottom aqueous phase. The reaction mixture was left to stand for 1 h to allow the phases to separate. The bottom aqueous layer was taken out with a syringe and purified by precipitation with acetone/DI water (8:1 respectively). This was centrifuged at 8,000 rpm for 10 min and the supernatant was decanted and the precipitate was redissolved in 2 mL DI H_2O. This was precipitated with acetone again and centrifuged at 8,000 rpm for 10 min. The supernatant was decanted and the precipitate was dissolved in DI H_2O and stored in the dark.

L- or D-cysteine-CdSe (Ø = 2.9 nm to Ø = 5.2 nm) were synthesized using similar reaction conditions as that of 2.5 nm L-cysteine-CdSe except that different sizes of OA-CdSe (with different concentrations) were used as starting material (see Table S2).

Table S2: *Concentrations of OA-CdSe in the ligand exchange synthesis of L-Cys-CdSe.*

Ø (OA-CdSe)	**[OA-CdSe]**
2.5 nm	0.030 mM
2.9 nm	0.019 mM
3.3 nm	0.014 mM

3.7 nm	0.011 mM
4.2 nm	0.0076 mM
4.5 nm	0.0061 mM
4.9 nm	0.0050 mM
5.3 nm	0.0039 mM

Table S3: *First excitonic band wavelengths (λ_{exc}, nm), diameters (Ø, nm) of OA-CdSe and L-Cys-CdSe and concentration of L-Cys-CdSe.*

λ_{exc} (OA-CdSe)	Ø (OA-CdSe)[a]	λ_{exc} (L-Cys-CdSe)	Ø (L-Cys-CdSe)[a]	[L-Cys-CdSe][b]
515.0 nm	2.5 nm	514.8 nm	2.5 nm	12.8 µM
543.0 nm	2.9 nm	543.0 nm	2.9 nm	8.58 µM
561.0 nm	3.3 nm	559.4 nm	3.2 nm	6.41 µM
575.6 nm	3.7 nm	574.2 nm	3.6 nm	4.74 µM
590.8 nm	4.2 nm	588.8 nm	4.1 nm	3.39 µM
599.4 nm	4.5 nm	596.2 nm	4.4 nm	2.83 µM
607.4 nm	4.9 nm	604.4 nm	4.8 nm	2.29 µM
616.0 nm	5.4 nm	613.4 nm	5.2 nm	1.80 µM

[a] The sizes were determined by using empirical fitting functions developed by Peng.[5] [b] Concentration during the CD, UV-vis and emission experiments corresponding to A_{exc} = 0.85.[5]

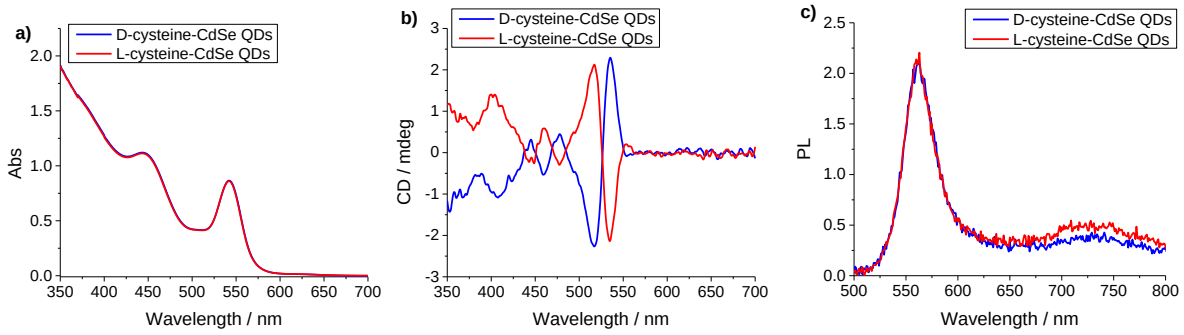

Figure S1: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 2.5 nm D-Cys-CdSe (blue curves) and Ø = 2.5 nm L-Cys-CdSe (red curves) QDs prepared from TOPO/OA-CdSe.

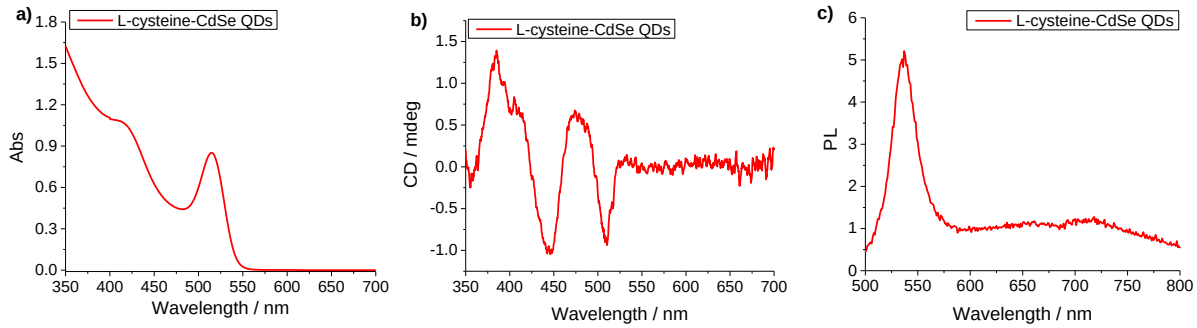

Figure S2: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 2.5 nm L-Cys-CdSe QDs prepared from OA-CdSe.

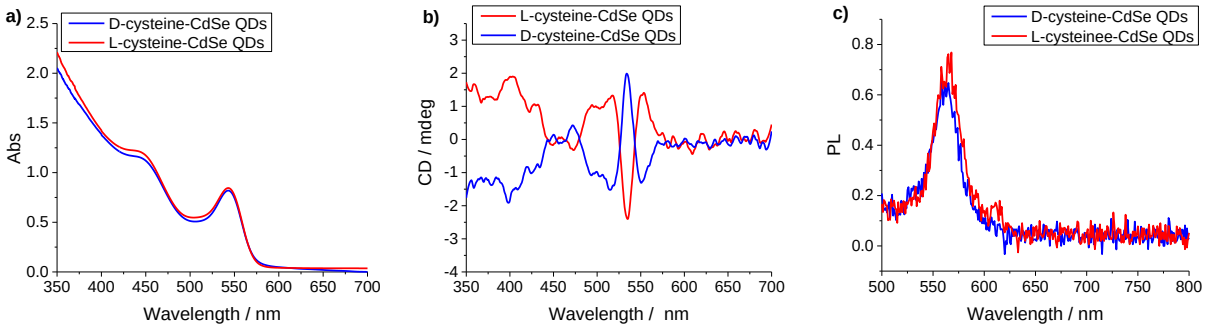

Figure S3: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 2.9 nm D-Cys-CdSe (blue curves) and L-Cys-CdSe (red curves) QDs prepared from OA-CdSe.

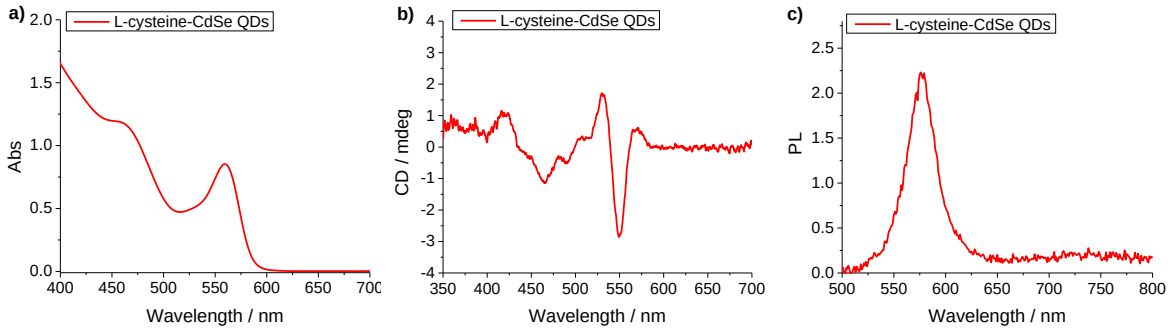

Figure S4: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 3.2 nm L-Cys-CdSe QDs prepared from OA-CdSe.

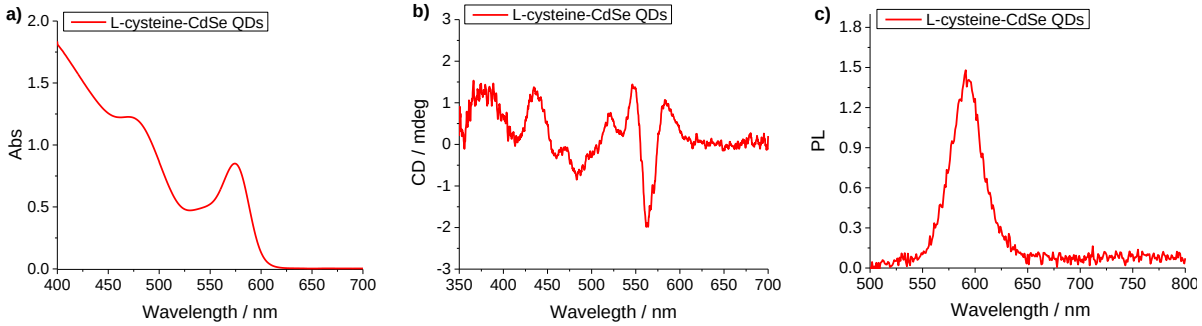

Figure S5: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 3.6 nm L-Cys-CdSe QDs prepared from OA-CdSe.

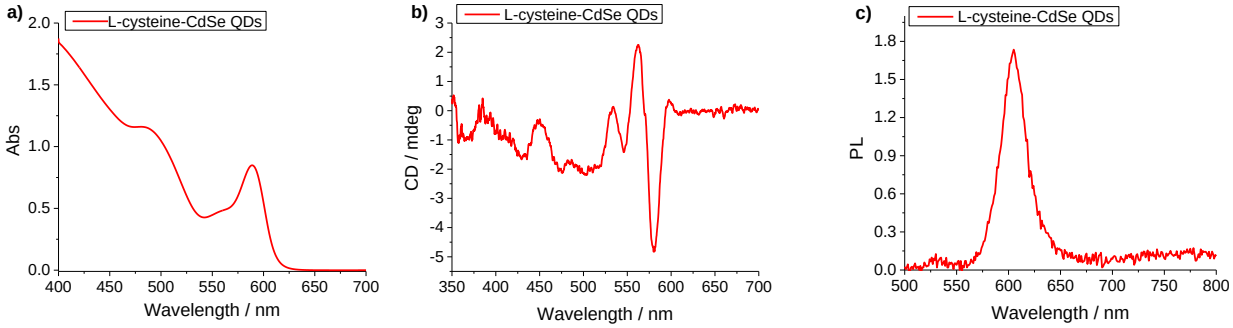

Figure S6: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 4.1 nm L-Cys-CdSe QDs prepared from OA-CdSe.

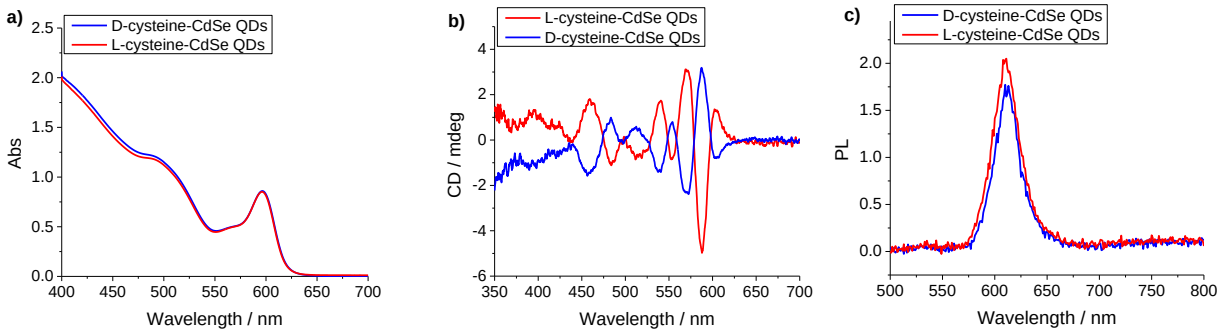

Figure S7: (a) UV-vis, (b) CD, and (c) fluorescence spectra of Ø = 4.4 nm D-Cys-CdSe (blue curves) and L-Cys-CdSe (red curves) QDs prepared from OA-CdSe.

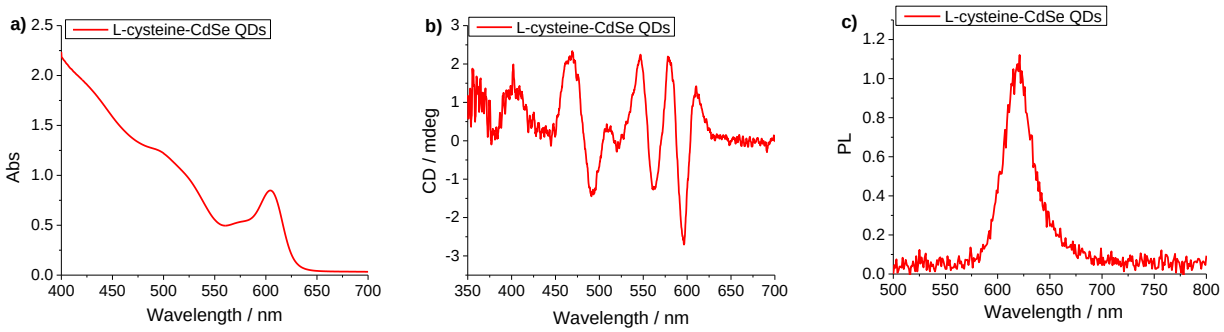

Figure S8: (a) UV-vis, (b) CD, and (c) fluorescence spectra of 4.8 nm L-Cys-CdSe QDs prepared from OA-CdSe.

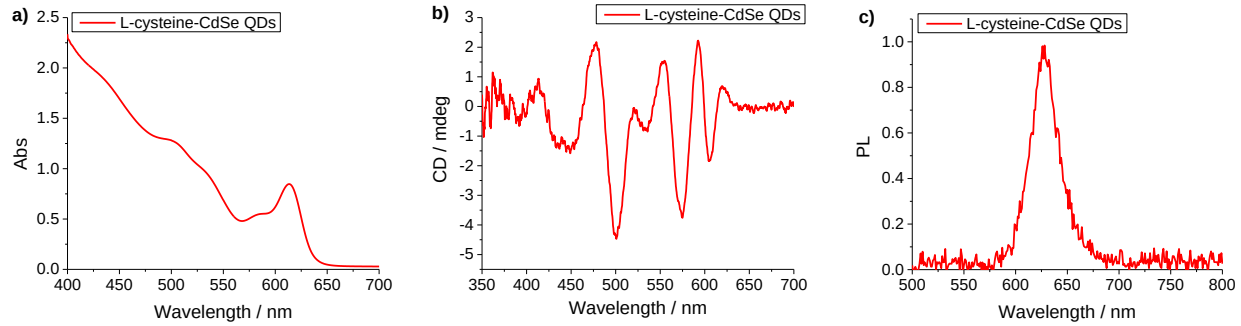

Figure S9: (a) UV-vis, (b) CD, and (c) fluorescence spectra of 5.2 nm L-Cys-CdSe QDs prepared from OA-CdSe.

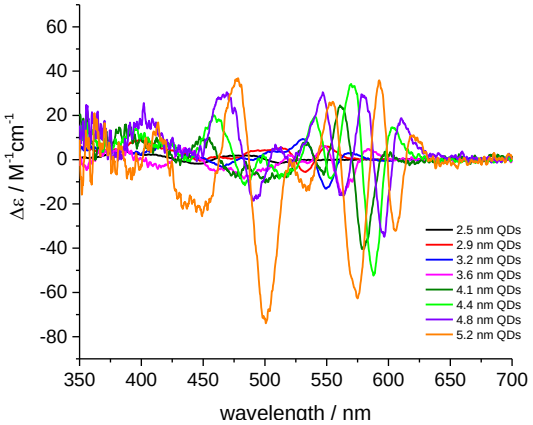

Figure S10: Molar CD spectra of 2.5 nm to 5.2 nm L-Cys-CdSe QDs.

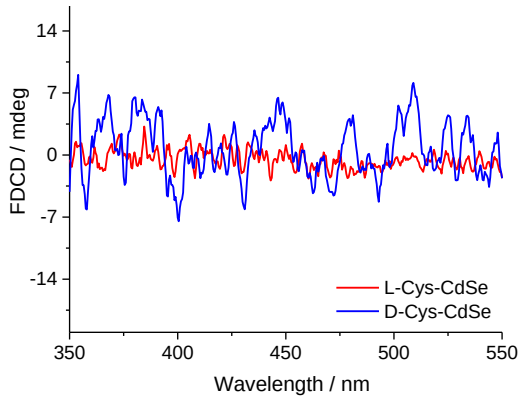

Figure S11: FDCD spectra of L-Cys-CdSe (red curve) and D-Cys-CdSe (blue curve) QDs (Ø = 2.9 nm) prepared from OA-CdSe.

Table S4. *Average geometric parameters for ($CdSe_{13}$ nanocluster optimized at PBEPBE/sbkjc-VDZ*/CPCM level in implicit water. Bond lengths (d) are in Å, valence angles (α) in degrees.*

Parameter	Average value
d(Cd(2)-Se)[a]	2.584
d(Cd(3)-Se)	2.69
d(Cd(4)-Se)	2.77
α(Se-Cd(2)-Se)	165
α(Se-Cd(2)-Se)	119
α(Se-Cd(2)-Se)	110
α(Cd-Se(3)-Cd)	81
α(Cd-Se(4)-Cd)	100

[a]The number in parentheses denotes coordination, e.g. Cd(2) is two-fold coordinated, Cd(3) three-fold etc.

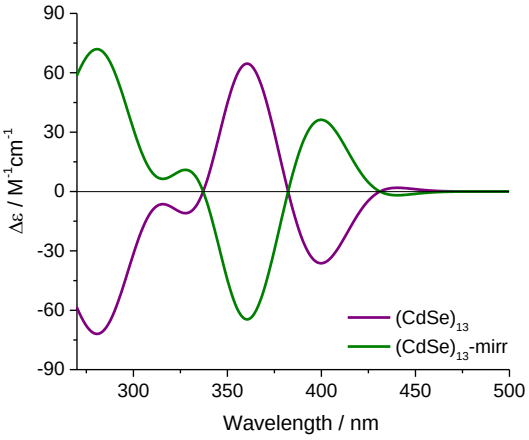

Figure S12: Calculated CD spectra of the optimized $(CdSe)_{13}$ cluster (purple curve) and the opposite enantiomer of $(CdSe)_{13}$ (green curve).

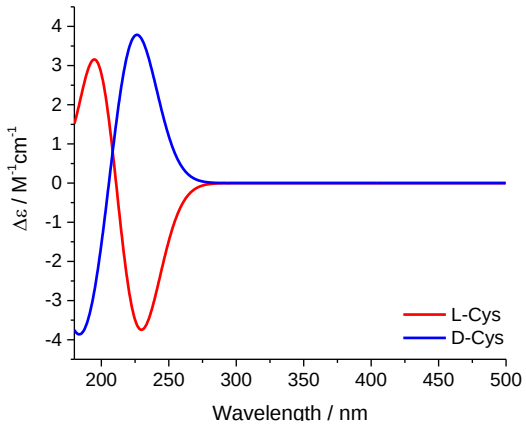

Figure S13: Calculated CD spectra of L-cysteine (red curve) and D-cysteine (blue curve).

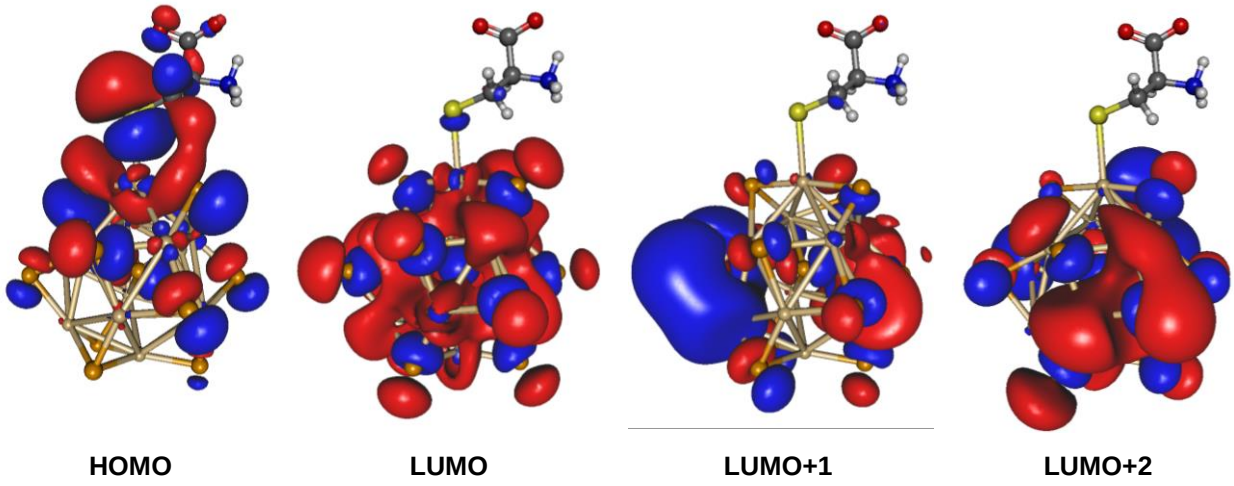

Figure S14: Calculated molecular orbitals of L-Cys-$(CdSe)_{13}$. Cys and $(CdSe)_{13}$ orbital hybridization is evident in HOMO.

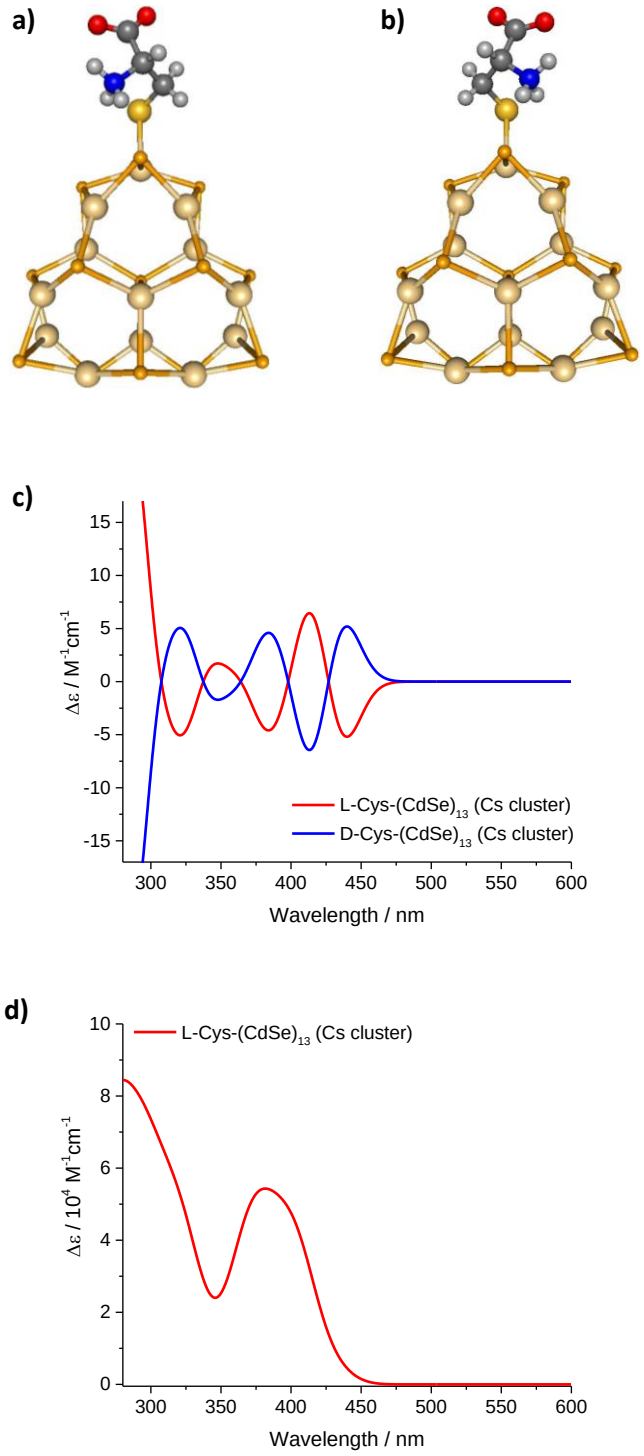

Figure S15: Simulation of the induced CD spectra for Cys-CdSe models with an alternative $(CdSe)_{13}$ cluster structure (with Cs symmetry). The calculations were carried out using the same methods as those described in the main text. (a) optimized geometry of L-Cys-$(CdSe)_{13}$ (b) optimized geometry of D-Cys-$(CdSe)_{13}$. (c) Simulated CD spectra for L-Cys-$(CdSe)_{13}$ (red) and D-Cys-$(CdSe)_{13}$ (blue). (d) Simulated

UV-vis spectra. Note the different shape of the UV exciton band compared to the minimum energy $(CdSe)_{13}$ clusters (Fig. 8) and a red shift of the center of the trisignate CD pattern with respect to the excitonic UV absorption maximum.

References

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